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Structural studies of Permian "Gondwana" coals of Barapukuria by infrared spectroscopy

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Abstract : Infrared spectroscopy is well suited for the characterization of highly absorbing materials particularly coal as it can provide information on both the organic and inorganic species of the coal matrix. The application of IR technique for the characterization of coal and mineral has been discussed in this paper. From the IR investigations Bangladeshi coals are revealed as higher rank of Bituminous type with high calorific value and low ash and minerals are basically silicious nature. Coal samples are carbonized at different temperatures under argon atmosphere and examined by IR. Under carbonization, increase in crystallite size or an increase in ordering of aromatic ring occurs, indicating the initial stage of graphitization. Stacking height and crystallite dimensions are also calculated by X-ray diffraction study.

Keywords : Infrared spectroscopy, bituminous coal, X-ray diffraction

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1. Introduction

Coal is an important natural resource and much effort has been given to make the best use of it. Fundamental scientific research has been going on for understanding the structure of coal for augmenting its technical use. The great potential of coal lies in its utilization in power and heat generation and in chemical industries.

Infrared spectroscopy has been a useful tool for studying coal structure since the first extensive investigation by Cannon and Sutherland [1]. Earlier works on coals includes structural study on coal and its different solvent extracts by IR using different techniques [2–6]. Painter *et al* [7] observed that there are four types of hydrogen-bonding that contributed to the cross-linking in the macromolecule network of coal structure and the presence of these bonding influenced the swelling property of coals. Kuehn *et al* [8] worked on quantitative determination of hydroxyl group and aromatic and aliphatic C–H groups in vitrinite concentrations using FT-i.r. spectroscopy.

Painter *et al* [9] in 1978 worked on quantitative mineralogical analysis of coals using fourier transform infrared technique. They determined the weight fractions of different minerals like kaolinite, quartz, gypsum, *etc*. in low temperature ash.

Coals which are rich in organic aromatic groups, exhibit higher rank. For chemical processing and extraction of organic groups from coal, the detailed structural study is necessary. In this regard infrared spectroscopy is well suited to study the structure of coal because it can be used to identify specific functional groups such as CH, C=O and O–H *etc*. In conjunction with IR, X-ray diffraction will be used for crystallite and mineral phase identification. The physical characterization of these coals will also be carried out employing proximate analysis. The objective of this research work is to study the quality of Barapukuria coal interms of organic and mineral matters.

2. Experimental

2.1. Coal sampling :

Coal samples have been collected systematically from different depths of boreholes GDH-38 and GDH-39 of Barapukuria coal mine with the help of Geological Survey of Bangladesh (GSB). Total area covered by this coal deposit is about 5.25 sq. km. Depth of coal-deposit ranges from 387 to 1600 feet below the surface. The total *in situ* geological reserve is estimated to be about 300 million metric tons. Twenty samples were collected from each borehole of GDH-38 and GDH-39 at different depths (from 400′ to 1400′). The samples have been reserved in airtight polythene bags.

2.2. Proximate analysis :

Proximate analysis of the Barapukuria coal samples was carried out according to ASTM standard D 3172 [10]. Moisture content, volatile matter content, ash content, fixed carbon content, calorific value and bulk density were determined under a set of standard conditions.

2.3. Infrared spectroscopy :

KBr technique developed by Scheidt [11] has been employed to take IR spectrum of the coal samples. KBr pellets were prepared by grinding ~3 mg of finely powdered raw coal with ~300 mg of potassium bromide in an agate mortar for 5 minutes and then pressing into pellet of 13 mm dia under 15000 psi pressure in a hand press pellet maker. The resulting thin and transparent pellets were dried over-night in a vacuum oven at 105°C and then stored in a desiccator until analysis.

2.4. X-ray diffraction of coal :

Diffraction analysis of coals has been carried out using an X-ray Diffractometer (JDX-8D, JEOL Co Ltd., Tokyo, Japan) at 30 KV operating voltage and 30 mA current. Coal samples were ground to 200 mesh (Tyler) size powder. d-spacing for [002] line was calculated using well known Bragg equation $2d_{hkl} \sin \theta_{hkl} = n\lambda$, where, $\lambda = 1.542$ Å, the wave length of Cu–K_α radiation and θ_{hkl} is position of [*hkl*] band on the diffraction curve and '*n*' is the

number of order (here $n = 1$). Crystallite dimension was determined using Blayden [12] formula. Layer diameter (L_a) has been calculated using the equation, $\beta = \frac{1.84\lambda}{L_a \cos\theta}$ where β is the full width at half-maximum intensity of the diffraction pattern and θ is the position of the [100] plane. Stack height parameter (L_a) has been calculated using the formula $\beta = \frac{1.00\lambda}{L_a \cos\theta}$ where β is the full width at half-maximum intensity of the diffraction pattern and θ is the position of the [002] plane.

2.5. Pyrolysis of coals :

Coal samples of borehole GDH-38 at depth 673′ were heat treated at 300°C, 400°C, 500°C, 600°C, 700°C and 900°C in a tubular furnace under argon atmosphere for 15 minutes.

3. Results and discussion

From analysis it was found that the coals are mostly high volatile A type bituminous with low moisture and low ash content. The data in Table 1 shows the results of proximate

Table 1. Proximate analysis of Barapukuria coal.

Bore hole	Depth (in feet)	Moisture (wt%)	Ash % db	VM % daf	F.C % daf	Calorific value Btu/lb daf	Bulk density kg/m^3	ASTM Rank
GDH-38	673	3.19	16 58	40 88	59.12	14296 64	1200	HvAb
	1102	2.46	10 25	42.73	57.27	15064.82	1400	HvAb
	1111	2.77	4.01	34 66	65.34	15205.53	1416	HvAb
	1121	2.43	4.40	41 84	58.16	15176.74	1280	HvAb
	1149	2.08	1.53	39.52	60.48	15136 20	1320	HvAb
	1161	3.24	5.79	33.97	66.03	15376.31	1312	HvAb
GDH-39	563	3.57	4.30	36.66	63 64	14507.10	1316	HvAb
	574	3.59	3.90	40.05	59.95	14749 75	1680	HvAb
	593	3.65	6.40	39.42	60.58	15513.45	1530	HvAb
	614	3.30	14.58	32.15	67.85	15081.98	1280	HvAb
	630	2.97	11.30	35.51	64.49	15841.72	1330	HvAb
	638	3.82	4.43	34.02	65.94	14575.28	1334	HvAb

db = dry basis; daf = dry ash free

analysis for the coal samples of borehole GDH-38 and GDH-39. The moisture content of the investigated samples are low and below 4 per cent for almost all of the samples. The ash content are minimal and varies from 1 to 16 per cent with an average of about 7.0 per cent for coals of bore-hole GDH-38 and about 7.5 per cent for coals of bore-hole GDH-39. The upper most layer of GDH-38 at depth 673 feet has the maximum ash content and the lower

most layers at 1149 feet has the minimum ash content. The GDH-39 bore-hole has the highest ash at the 614 feet layer.

The volatile matter content and calorific value of the samples show that the Barapukuria coals are high volatile bituminous types. The volatile matter content of GDH-38 samples varies from 32 to 40 per cent and those of GDH-39 samples varies from 31 to 38 per cent on dry basis (db). The fixed carbon content of GDH-38 samples varies from 57 to 66 per cent.

3.1. Results of IR spectroscopy :

The IR spectra of different coal samples show simillar results and suggest similar carbon skeleton, functional group and mineral matters present in coal. The spectra for the coals of GDH-38 and GDH-39 are shown in Figures 1 and 2.

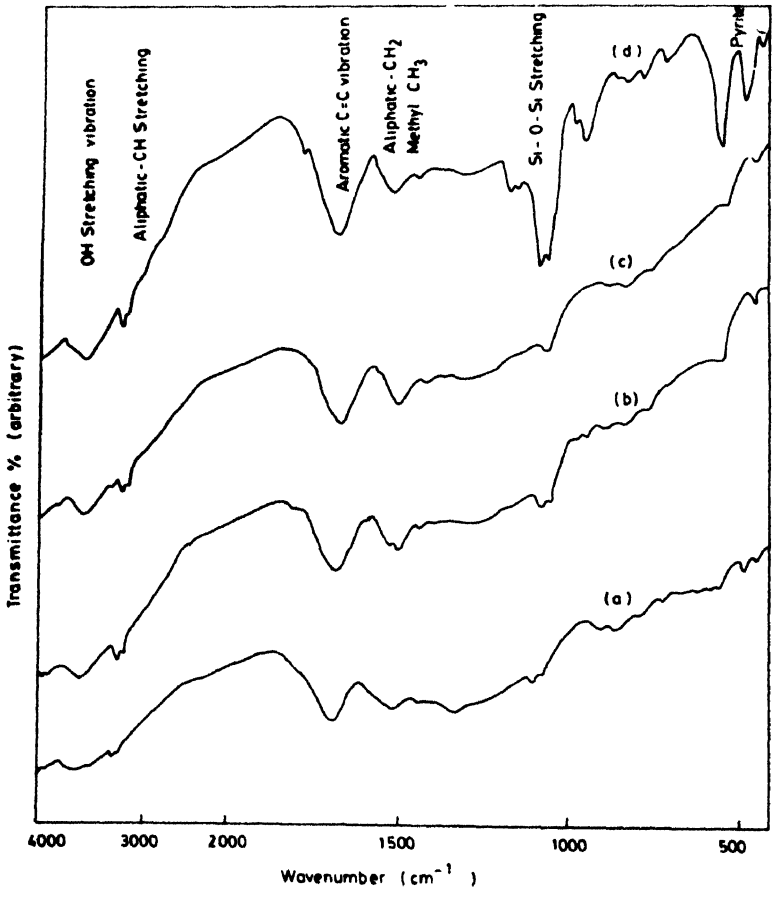

Figure 1. Infrared spectrum of Barapukuria coals of borehole GDH-38 : (a) d-563', (b) d-1121', (c) d-1149', (d) d-1102'.

The common feature of all the spectra is the sloping of the base line toward the higher frequency (about 1000 cm^{-1}). The sloping is due to scattering of transmitted radiation by coal particles in KBr pellets.

All the spectra suggest higher degree of aromaticity of the samples that can be inferred from the bands between 3000 and 3100 cm^{-1} and between 900 and 700 cm^{-1}. The aromatic C–H stretching region at 3050 cm^{-1} might be overlapped by broad OH absorption band around at 3300 cm^{-1}. The band around at 2920 cm^{-1} is due to anti-symmetric C–H stretching modes of methylene group and the band near at 2850 cm^{-1} is due to aliphatic C–H stretching mode. These two bands suggest the presence of aliphatic hydrogen species.

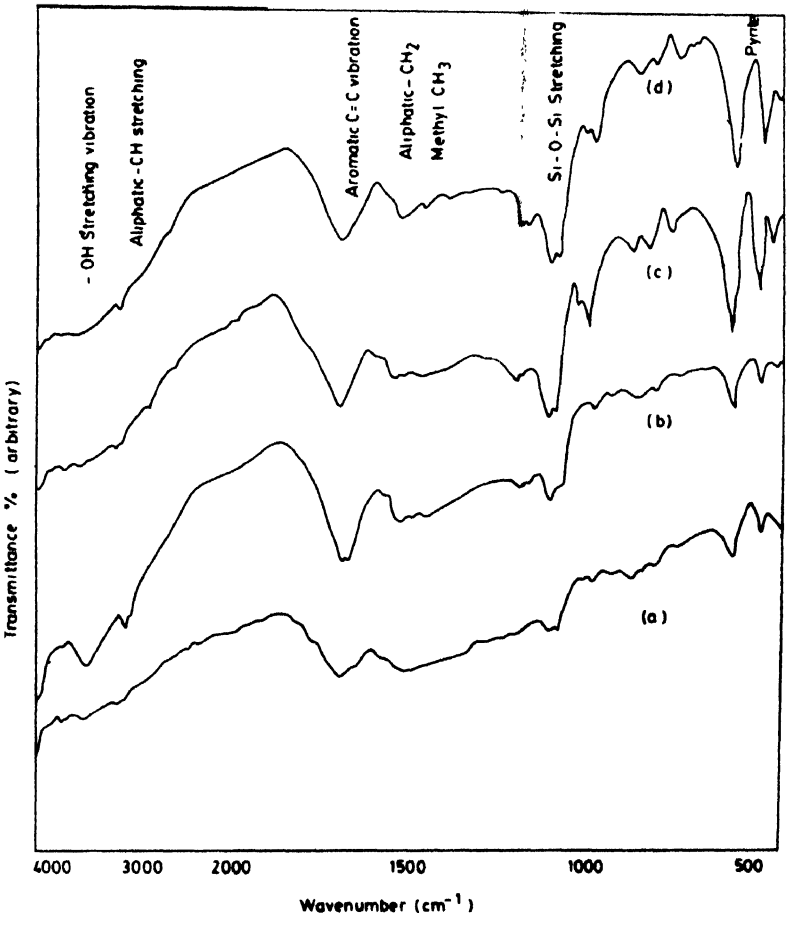

Figure 2. Infrared spectrum of Barapukuria coals of borehole GDH-39 : (a) d 574', (b) d-593', (c) d-614', (d) d-630'.

The large absorption band near at 1600 cm^{-1} is indicative of condensed polynuclear atomatic ring vibration [13–16]. The intensity of this band is assumed to be enhanced by the presence of hydroxyl group on the ring and nitrogen in the ring. The bands at 1400 and 1370 cm^{-1} indicate the presence of methyl CH_2 and aliphatic methylene (CH_3) respectively. The higher absorption in the region 1400 cm^{-1} suggests that the coals of GDH-38 and GDH-39 are composed of fewer aliphatic methylene group than methyl. A pronounced band at 1030 cm^{-1} in all of the spectra indicates the presence of kaolinite in all the samples.

The aromatic wag region is made-up of three primary peaks at 870, 817 and 753 cm^{-1} corresponding to one isolated two adjacent and four adjacent aromatic C–H group [17]. The 870 cm^{-1} band due to isolated C–H wagging in condensed aromatic ring is indicative of higher degree of aromatic ring condensation. There are also some other mineral peaks at 540 cm^{-1} and 460 cm^{-1} due to kaolinite and at 435 and 410 cm^{-1} due to pyrites in the spectra of different samples.

IR spectra of carbonized coals are shown in Figure 3. A little change is observed in spectra of coals heated to 300°C. Intensity of band at 3400 cm^{-1} is found to decrease due to loss of water and other hydroxylic matter. The 900 to 700 cm^{-1} region remains unchanged.

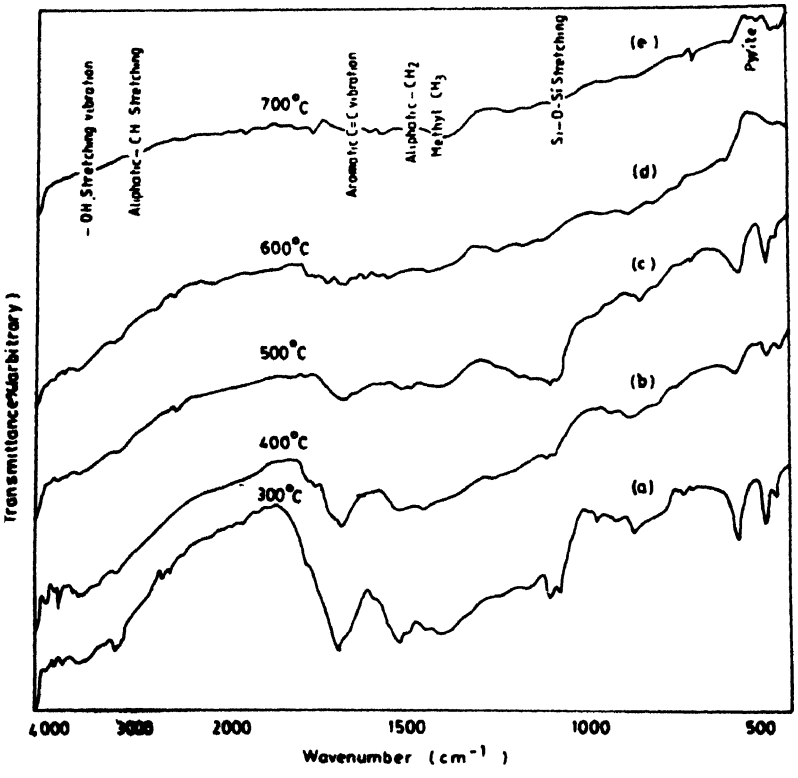

Figure 3. Infrared spectrum of carbonized coals of borehole GDH-38 : (a) carbonized at 300°C, (b) carbonized at 400°C, (c) carbonized at 500°C, (d) carbonized at 600°C, (e) carbonized at 700°C/15 mins.

At 500°C a pronounced decrease in the absorption band at 3400 cm^{-1} is due to loss of OH is observed. Aromatic C=C stretching vibration band is found to shift toward 1580 cm^{-1}. This is due to conjugation of aromatic rings and removal of aliphatic chains. The mineral band at 1030 cm^{-1} is also found to decrease. An observable phenomena in the 500°C spectra is the overall increase of background absorption.

Structureless background absorption extends throughout the 4000 to 400 cm^{-1} region for coal samples carbonized above 500°C which means that the chars have become opaque in the infrared. This suggests that above 500°C some graphitization has occurred which is

supported by XRD data that there is an increase in crystallite size or an increase in ordering of aromatic rings.

3.2. X-ray diffraction :

The X-ray diffractograms of the coals are continuous curves with an initial broad peak between 4 and 14° (2θ) on which more or less diffuse peaks are superimposed, indicating

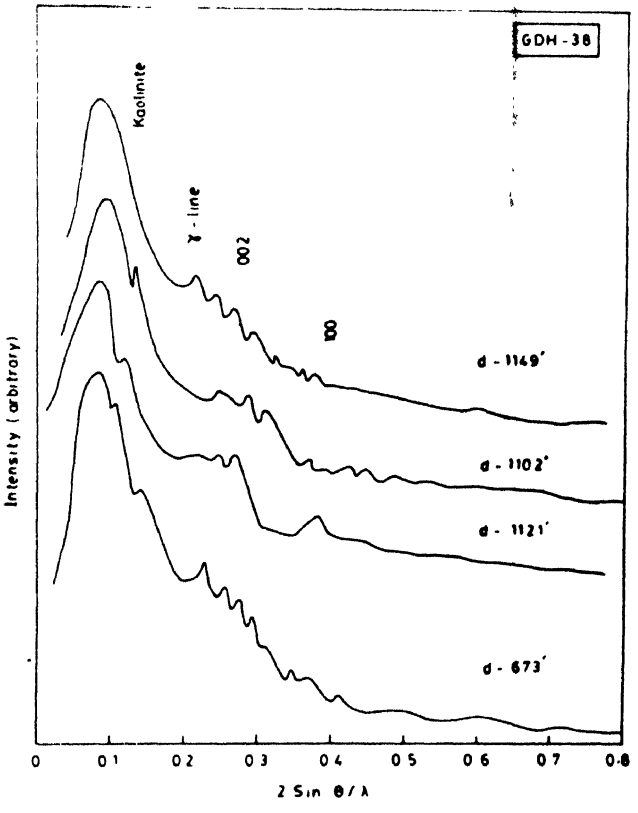

Figure 4. X-ray diffraction of coal samples of GDH-38.

the largely amorphous nature of coal. There are some small peaks throughout wide-angle region ($S = 2 \sin \theta / \lambda \geq 0.15$ Å^{-1}) which are due to micro-crystallites of ordered aromatic lamellae and due to different mineral phases. X-ray diffractograms for coals of borehole GDH-38 and GDH-39 are shown in Figures 4 and 5. The results are summarized in Table 2.

A peak at 12° (2θ) superimposed on the left side of initial broad peak is identified as reflection from kaolinite which is accompanied by a peak at 25° (2θ). There are some other diffused peaks throughout the wide-angle region that might be reflections from different minerals such as quartz, pyrite *etc.*

A diffuse peak between 24 and 26° (2θ) can be observed in all of the diffractograms which is identified as *c*-peak [12,18] and is caused by reflections from planes stacked

nearly parallel to each other. These weak peaks indicate poorly ordered regions within the coal matrix. Stacking of planer sheets formed by substitution of aromatic rings forms the

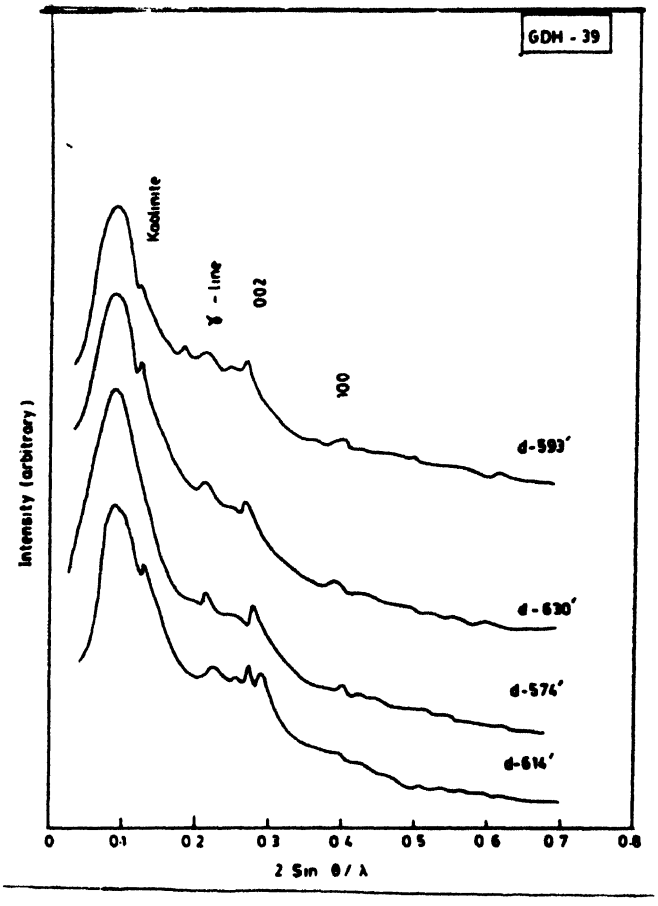

Figure 5. X-ray diffraction of coal samples of GDH-39.

Table 2. X-ray analysis of Barapukuria coal.

Bore hole	Depth in feet	002 line deg	d_{002} Å	100 line deg	d_{100} Å	γ-line deg	$d\gamma$ Å	β_{002} deg	L_c Å	β_{100} deg	La Å
GDH-38	673	26.1	3.41	38.0	2.37	20.6	4.31	8	11.30	9	19.21
	1102	24.7	3.60	38.2	2.38	18.4	4.82	8	11.30	8	21.50
	1121	24.4	3.64	35.4	2.58	20.5	4.33	6	15.06	8	21.33
	1149	24.4	3.64	37.8	2.38	20.2	4.40	6	15.06	9	19.09
GDH-39	574	24.5	3.63	38.2	2.36	19.1	4.42	6	15.06	8	21.50
	593	24.4	3.64	38.6	2.33	20.0	4.44	6	15.06	8	21.53
	614	26.6	3.35	38.2	2.36	20.6	4.31	6	15.13	8	21.50
	630	24.4	3.64	35.4	2.58	20.2	4.40	6	15.06	—	—

ordered regions. The stack height parameter (L_c) calculation following Blayden *et al* [12] formula shows L_c to lie between 11 to 15 Å. Thus there can be 3 to 4 layers stacked parallel to each other. The γ-peak, caused by reflections from buckled aromatic sheets or aliphatic materials [19] is identified around 20° (2θ) with d-values around 4.44 Å. A small peak around 33° with d-values 2.73 Å is due to reflections for crystallites of pyrites or marcasites [20].

Another peak around 35° is identified as cross lattice line that is a-peak. This peak is caused by reflections from individual hexagonal (aromatic) planes acting as two-dimensional gratings. The layer diameter determined from these peaks are about 20 Å. The layer diameter and stack height parameter determined from broadening of a-peak and c-peak respectively are not true dimensions of crystallite region, rather they are related to the degree of coherence of planar layer.

X-ray diffractograms of carbonized coals are shown in Figure 6 and the results are summarized in Table 3. The diffractograms show a clear and sharp appearance of 002 line

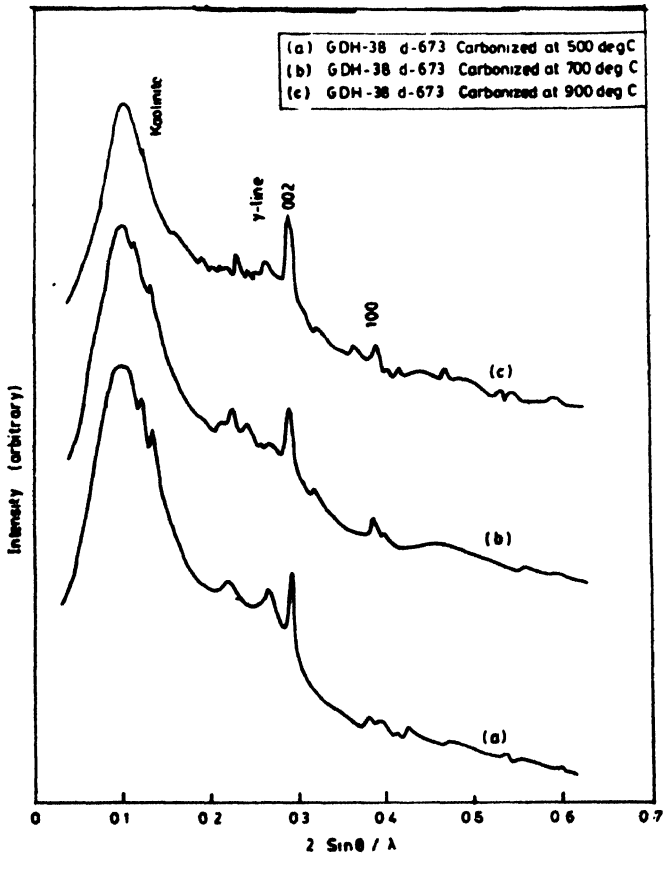

Figure 6. X-ray diffractograms of carbonized coals of GDH-38 D-673' : (a) 500°C/15 ; (b) 700°C/15 min, (c) 900°C/15 min.

for the coal samples carbonized at 300°C. This is a clear indication of increase of ordering between planar aromatic layers. The sharpness and peak height of the line is found to increase with temperature. From calculation, it is found that the stacking height parameter

Table 3. X-ray analysis of carbonized coal.

Sample	Temp. °C	002 line deg	d_{002} Å	100 line deg	d_{100} Å	γ-line deg	$d\gamma$ Å	β_{002} deg	L_c Å	β_{100} deg	La Å
GDH-38	Raw	26.1	3.41	38.0	2.37	20.6	4.31	8	11.30	9	19.21
	300	26.3	3.39	38.4	2.34	19.2	4.62	6	15.10	8	21.51
	500	26.1	3.41	37.8	2.38	20.5	4.33	4	22.00	8	21.47
	700	26.3	3.39	35.0	2.56	18.5	4.79	5	18.10	7	24.35
	900	26.2	3.41	35.0	2.56	20.6	4.32	4	22.00	6	28.40

increases from 11 Å to 22 Å and the layer diameter increases from 19 Å and 28 Å thus producing to some extend the graphitization.

4. Conclusions

The following conclusions may be drawn from the present study. The Barapukuria coals under study are ranked mainly as high volatile bituminous type with high calorific value and low ash. IR spectroscopic study shows that the considerable portion of coal structure is aromatic in nature formed by planar graphitic sheet arranged nearly parallel to each other. X-ray diffraction of these coal samples determines the size of the crystalline region from the stack-height parameter and layer diameter calculation. Mineral phases of kaolinite, pyrites, *etc.* are also identified. A greater degree of orientation of the aromatic rings in the carbonized coal samples indicates the trend of graphitization process.

References

[1] C G Cannon and G B B M Sutherland *Trans. Faraday Soc.* **41** 279 (1944)

[2] G B B M Sutherland, P B Fellget and H A Wills *Proceeding of Conference on Ultrafine Structure of Coals and Cokes* (BCURA, London) p 330 (1945)

[3] M Orchin, C Golumbic, J E Anderson and H H Storch, *U S Bureau of Mines Bull* 505 (1951)

[4] R A Friedel and M G Pelipetz *J. Opt. Soc. Am.* **43** 1051 (1953)

[5] H H Storch *Melchett Lecture Inst. of Fuel* (1954); *J. Inst. Fuel* **28** 154 (1958)

[6] R R Gordon, W N Adams and G I Jenkins *Nature* **170** 317 (1952)

[7] P C Painter, M Sobkowiak and J Youtcheff *Fuel* **60** 973 (1987)

[8] W Debbie Kuehn, W Randy Synder, A Davis and P C Painter *Fuel* **61** 682 (1991)

[9] P C Painter, M Michael Coleman, G Robert Jenkins, W Pyung Whang and L Philip Walker (Jr) *Fuel* **57** 337 (1978)

[10] *American Society for Testing and Materials, Annual Book of ASTM Standards, Part 26* (Philadelphia) (1980)

[11] U Scheidt *Appl. Spectros.* **7** 75 (1953)

[12] H E Blayden, J Gibson and H L Riley *Proc. of the Conference on Ultrafine Structure of Coals and Cokes* (BCURA, London) p 176 (1943)

[13] H S Rao, P L Gupta, F Kaiser and A Lahiri *Fuel* **41** 417 (1962)

[14] R M Elofson and K E Schulz *Am. Chem. Soc. Div. Fuel Chem. Prepr.* **11** 513 (1967)

[15] R A Friedel, J A Queiser and G L Carlson *Am. Chem. Soc Div Fuel Chem Prepr.* **15(1)** 123 (1971)

[16] P C Painter, M Starsinic, E Squires and A Davis *Fuel* **62** 742 (1983)

[17] P R Solomon and R M Carangelo *Fuel* **67** 949 (1988)

[18] L Schoening *E. R Fuel* **62** 1315 (1983)

[19] C Mahadevan *Indian J. Phys.* **4** 79 (1929)

[20] M H Mazza and J S Wilson *Advances in X-ray Analysis* (New York : Plenum) **Vol 20** 431 (1976)